Homologation of alpha-olefins with ethene by a neutral zirconium alkyl complex

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Supporting Information to:

Homologation of Alpha-Olefins with Ethene by a Neutral Zirconium Alkyl Complex

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Experimental

All experiments were performed under nitrogen atmosphere using standard glove-box and Schlenk techniques. Deuterated solvents (Aldrich) were dried on molecular sieves, stored and used in a glove-box. Other solvents were either dried over sodium wire or distilled from sodium benzophenone ketyl. Ethene and propene (Scott, 99.5%) were used without further purification. 1-Pentene (Merck) was degassed, dried on molecular sieves and vacuum transferred, and subsequently kept and used in a drybox. $(C_6H_{10})Mg.THF$ was prepared according a simplified version of the published procedure (reaction performed at ambient temperature with intermittent shaking).[1] Cp^*MCl_3 (M = Zr, Hf; Strem) were used as purchased. $Cp^*Hf(C_6H_{10})Cl$ was prepared according to published procedure.[2] GC analyses were performed on a HP 5880A chromatograph with a CPSil 5 CB capillary column. The C_n linear olefins were identified by their retention times based on comparison with authentic samples up to C_{16}. NMR spectra were recorded on a Varian VXR-300 instrument (^1H: 300 MHz; ^{13}C: 75.4 MHz)

Synthesis of $Cp^*Hf(C_6H_{10})(n\text{-Bu})$. A solution of $Cp^*Hf(C_6H_{10})Cl$ (0.154 g, 0.357 mmol) was dissolved in 15 mL of diethyl ether. At -10°C 0.22 mL of a 1.6M *n*-BuLi solution in hexane was added in portions using a 50 µl syringe. After 15 min. the mixture was allowed to warm to

ambient temperature and stirred for 1 h. The solvent was removed *in vacuo* and the resulting sticky yellow mixture stirred with some pentane that was subsequently pumped off. The residue was extracted with pentane and the extract filtered after which the solvent was pumped off. The yellow oily product was dried *in vacuo* for an extended period. Crude yield 0.12 g (0.26 mmol, 74%, not optimised) The product eventually solidified after days at -40°C, but the compound is very soluble in pentane and could not be crystallised. By NMR the only visible impurities are traces of remaining solvent.

Synthesis of $Cp^*Zr(C_6H_{10})(n\text{-}Bu)$. The reported preparation of $Cp^*Zr(C_6H_{10})Cl$ gives a rather low yield.[2] The Zr-butyl complex was therefore synthesized using a two-step reaction starting from Cp^*ZrCl_3. To a solution of Cp^*ZrCl_3 (0.125 g, 0.375 mmol) in 8 mL of THF a solution of $(C_6H_{10})Mg.THF$ (67 mg, 0.375 mmol) was added at room temperature. The resulting red solution was stirred for 1 h, after which the solvent was removed *in vacuo*. The purple-red solid was then suspended in diethyl ether and 0.23 mL of a 1.6M *n*-BuLi solution in hexane was added in portions at ambient temperature using a 50 µl syringe. This gives a brown-orange solution with a fine light precipitate. After 15 min the solvent was pumped off and the sticky mixture stirred with some pentane that was subsequently pumped off (to remove residual ethers). The residue was extracted with pentane. After filtration of the extract and removal of the solvent *in vacuo*, the brown-orange oily product was dried for an extended period. Crude yield 90 mg (0.25 mmol, 66%, not optimised). Just like the Hf-analogue, the compound is highly soluble and could not be crystallised. By NMR the only visible impurities are traces of remaining solvent.

Reaction of $Cp^*Zr(C_6H_{10})(n\text{-}Bu)$ with portions of ethene A solution of $Cp^*Zr(C_6H_{10})(n\text{-}Bu)$ (13.0 mg, 0.035 mmol) in d_6-benzene was placed in an NMR-tube equipped with a rubber septum. A portion of ethene gas (2.4 ml, corresponding to approx. 0.10 mmol) was added by gas-tight syringe, followed by occasional shaking. Progress of the reaction was monitored by NMR. After full consumption of the ethene (<15 minutes) a sample was drawn for GC

analysis. The procedure was then repeated twice on the same NMR-tube sample with portions of 1.6 ml ethene.

Reaction of Cp*M(C_6H_{10})(*n*-Bu) with propene To a solution of Cp*Zr(C_6H_{10})(*n*-Bu) (3.0 mg, 8.2 μmol) in d_6-benzene in an NMR tube equipped with a rubber septum an excess of propene (2.5 mL gas, 0.11 mmol) was added by gas-tight syringe. The solution was warmed at 50°C in an oil bath. After 13 min. conversion to Cp*Zr(C_6H_{10})(*n*-Pr) and 1-butene was complete, as seen by ^{1}H-NMR spectroscopy. A similar experiment with the Hf-analogue also showed smooth conversion to the *n*-Pr-complex.

Stepwise homologation of 1-pentene with ethene A solution of Cp*Zr(C_6H_{10})(*n*-Bu) (18 mg, 0.049 mmol) and 1-pentene (50 μl, 0.46 mmol) in 0.65 ml of C_6D_6 was placed in an NMR-tube and sealed with a rubber septum. Then 1.7 ml of ethene (approximately 1.5 equiv. C_2H_4 per Zr) was added by gas-tight syringe. The progress of the reaction was monitored by NMR. After consumption of the ethene (10-15 minutes) the mixture was warmed to 50°C (10 min.). Subsequently a GC sample was taken. This procedure was repeated four times with similar amounts of ethene.

Reaction of Cp*Hf(C_6H_{10})(*n*-Bu) with ethene To a solution of Cp*Hf(C_6H_{10})(*n*-Bu) (3 mg, 6.7 μmol) in C_6D_6 in an NMR-tube equipped with a rubber septum, an excess of ethene (3 mL gas, 0.13 mmol) was added by gas-tight syringe. The reaction proceeded slowly under occasional shaking to give (after 15 h, by ^{1}H-NMR): Cp*Hf(C_6H_{10})Et (>70%), Cp*Hf(C_6H_{10})[$(CH_2CH_2)_n$Et] (<30%) and α-olefins (NMR, GC). The diene ligand resonances of the Hf-Et species on the one hand, and the higher *n*-alkyl derivatives on the other, are sufficiently well separated to allow a determination of their ratio by integration.

Catalytic oligomerisation of ethene with Cp*Hf(C_6H_{10})Et A solution of Cp*Hf(C_6H_{10})Et in benzene (4.10^{-3} M, 15 mg catalyst used) was placed in a stainless-steel autoclave (internal

volume 25 ml) with a Teflon-coated stirbar. The autoclave was placed in a thermostated oil bath at 100°C and allowed to equilibrate for 5 minutes. Ethene pressure (39 bar) was admitted and occasionally brought back up to original pressure during the run. Run times was 3 h. At the end of the run, the reactor was cooled in an ice bath, vented, and the mixture recovered for GC analysis. Hexylbenzene was added as standard for GC determinations. Relative product ratios of the various olefins (for $[C_{n+2}]/[C_n]$-factor) were estimated from integrated intensity divided by the number of carbon atoms in the chain. Quantitative calibration (with response factors deduced from calibration mixtures of 1-hexene and isomers) was used to determine the amount and purity of the C_6-fraction (99.6% 1-hexene, 0.2% 2-hexene, 0.2% 2-ethyl-1-butene + *n*-hexane).

Preparation and isomerisation of $Cp^*M(C_6H_{10})(i\text{-Pr})$ Small quantities of the iso-propyl complexes were prepared in NMR-tubes in d_6-benzene as follows: At ambient temperature solutions of $Cp^*Hf(C_6H_{10})Cl$ (20.5 mg, 0.047 mmol) and *i*-PrLi (2.3 mg = 0.046 mmol) in C_6D_6 were mixed to give a bright yellow solution with a white precipitate. The precipitate was centrifuged off to leave a clear solution for NMR measurements on the alkyl group isomerisation. Progress of the *i*-Pr/*n*-Pr ration was followed at 25°C by ^{1}H-NMR. The rate constant was estimated, assuming a first-order reaction, to be 2.6 (1) . 10^{-4} s^{-1} (corresponding to a half-life time of 46 min.).

For M = Zr, equimolar amounts (0.05 mmol) of Cp^*ZrCl_3 and $(C_6H_{10})Mg.THF$ were suspended in C_6D_6. After about 10 minutes a red clear solution had formed. Addition of 0.05 mmol of *i*-PrLi in C_6D_6 produced a cloudy orange-red solution that was subsequently centrifuged. The isomerisation reaction at 25°C is quite rapid, and only an estimate of the rate constant could be made (9.10^{-4} s^{-1}, corresponding to a half-life time of about 13 min.).

Characterisation of the complexes $Cp^*M(C_6H_{10})$(alkyl).

The full characterisation of the new $Cp^*M(C_6H_{10})$(alkyl) derivatives reported is hampered by the physical characteristics of the compounds. They are extremely soluble in organic solvents

and could not be crystallised. Evaporation of the solvent from solutions of the compounds persistently enclose sub-stoichiometric amounts of solvent, making elemental analysis useless as method of characterisation. Cooling these oils to -40°C causes them to solidify in time, but the melting points of these extremely air- and moisture-sensitive compounds are below room temperature, making them awkward to handle. The compounds do not stand up to conditions for mass-spectroscopic characterisation. Therefore we have to rely on NMR spectroscopy for characterisation of these compounds, and on comparison with the known related complexes Cp*Hf(C_6H_{10})Cl, Cp*Hf(C_6H_{10})Me, Cp*Hf(C_6H_{10})Et and Cp*Zr(C_6H_{10})Cl that have been characterised by elemental analysis and were found to be monomeric by cryoscopic molecular weight determination and by single crystal X-ray diffraction (of Cp*Hf(C_6H_{10})Cl), as reported in ref. 2 below (ref. 5b of the manuscript). The features of the ^{1}H- and ^{13}C-NMR spectra of the new compounds are fully consistent with those expected for substitution of the chloride in Cp*M(C_6H_{10})Cl by an alkyl group. For example, in the ^{1}H-NMR spectra this leads consistently to a small upfield shift of the *endo*-methylene protons of the diene and a small decrease of the $^2J_{HH}$ of this group, and in the ^{13}C-NMR spectra to an upfield shift of the diene methylene carbon resonances. These features were also observed in the alkyl derivatives reported in ref.2 below (is ref 5b in the manuscript). The NMR-spectroscopic features of the *n*-Bu groups of **1** and **2** are consistent with non-agostic and fluxional β-agostic structures respectively. The multiplet structures of the alkyl ^{1}H-NMR resonances of Cp*Hf(C_6H_{10})(*n*-Pr) and Cp*Hf(C_6H_{10})(*i*-Pr), the latter complicated by the small chemical shift difference between the α- and β-protons, could be reproduced by simulation (although the resolution of the experimental spectra did not allow an accurate determination of all the pertaining coupling constants). The NMR-data of the new reported compounds are given below (C_6D_6 solvent, 25°C , ^{1}H: 300 MHz; ^{13}C: 75.4 MHz).

Cp*Hf(C_6H_{10})(*n*-Bu) (**1**). ^{1}H-NMR: δ 2.19 (s, 6H, diene-Me), 1.95 (s, 15H, Cp*, overlapping *syn*-CH_2), 1.34 (ps.sextet, 7.1 Hz, 2H, γ-CH_2), 0.94 (t, 7.2 Hz, 3H, δ-CH_3), 0.17 (m, 2H, β-CH_2), -0.03 (m, 2H, α-CH_2), -0.15 (d, 9.9 Hz, 2H, *anti*-CH_2). ^{13}C-NMR δ 11.31 (q, 126 Hz, Cp*Me),

14.65 (q, 124 Hz, δ-CH_3), 22.37 (t, 120 Hz, β-CH_2), 23.75 (q, 126 Hz, diene-Me), 28.13 (t, 124 Hz, γ-CH_2), 64.25 (t, 117 Hz, α-CH_2), 65.10 (dd, 132 Hz, 146 Hz, diene-CH_2), 117.21 (s, Cp* ring), 125.28 (s, =*C*(Me)-).

$Cp^*Zr(C_6H_{10})$(*n*-Bu) (**2**). ^{1}H-NMR: δ 2.11 (d, 8.8 Hz, 2H, *syn*-CH_2), 2.00 (s, 6H, diene Me), 1.92 (s, 15H, Cp*), 1.35 (ps.sextet, 7Hz, 2H, γ-CH_2), 0.94 (t, 7.3 Hz, 3H, δ-CH_3), 0.32 (overlapped, 2H, *anti*-CH_2), 0.30 (m, 2H, α-CH_2), -0.82 (m, 2H, β-CH_2). ^{13}C-NMR δ 11.69 (q, 126.1 Hz, Cp*-Me), 15.14 (q, 124.8 Hz, δ-CH_3), 20.37 (t, 113.8 Hz, β-CH_2), 23.63 (q, 125.7 Hz, diene-Me), 27.19 (t, 124.8 Hz, γ-CH_2), 53.94 (t, 127.7 Hz, α-CH_2), 59.80 (dd, 139.0 Hz, 150.7 Hz, diene-CH_2), 117.10 (s, Cp*-ring), 125.64 (s, =*C*(Me)-).

$Cp^*Hf(C_6H_{10})$(*n*-Pr). ^{1}H-NMR: δ 2.17 (s, 6H, diene-Me), 1.94 (s, 15H, Cp*), 1.92 (d, 10.0 Hz, 2H, *syn*-CH_2), 1.05 (t, 6.9 Hz, 3H, γ-CH_3), 0.30 (m, 2H, β-CH_2), -0.04 (m, 2H, α-CH_2), -0.17 (d, 10.0 Hz, 2H, *anti*-CH_2).

$Cp^*Zr(C_6H_{10})$(*n*-Pr). ^{1}H-NMR: δ 2.10 (d, 8.7 Hz, 2H, *syn*-CH_2), 1.99 (s, 6H, diene-Me), 1.91 (s, 15H, Cp*), 1.07 (t, 6.7 Hz, 3H, γ-CH_3), 0.30 (d, 8.6 Hz, 2H, *anti*-CH_2), overlapping with 0.30 (m, 2H, α-CH_2), -0.77 (m, 2H, β-CH_2).

$Cp^*Hf(C_6H_{10})$(*i*-Pr). ^{1}H-NMR: δ 2.11 (s, 6H, diene-Me), 1.91 (s, 15H, Cp*), 1.86 (d, 10.5 Hz, 2H, *syn*-CH_2), 0.53 (br.d, ≈7 Hz, 6H, β-CH_3), 0.34 (m, 1H, α-CH), -0.11 (d, 10.5 Hz, 2H, *anti*-CH_2).

$Cp^*Zr(C_6H_{10})$(*i*-Pr). ^{1}H-NMR: δ 2.16 (d, 8.4 Hz, 2H, *syn*-CH_2), 1.93 (s, 6H, diene-Me), 1.88 (s, 15H, Cp*), 0.58 (septet, 7.6 Hz, 1H, α-CH), 0.40 (d, 8.4 Hz, 2H, *anti*-CH_2), 0.04 (d, 7.6 Hz, 6H, β-CH_3).

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